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Transition energies of mercury and ekamercury (element 112) by the relativistic coupled-cluster method

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The relativistic coupled-cluster method is used to calculate ionization potentials and excitation energies of Hg and element 112, as well as their mono- and dications. Large basis sets are used, with l up to 5, the Dirac-Fock or Dirac-Fock-Breit orbitals found, and the external 34 electrons of each atom are correlated by the coupled-cluster method with single and double excitations. Very good agreement with experiment is obtained for the Hg transition energies, with the exception of the high (>12 eV) excitation energies of the dication. As in the case of element 111 [Eliav *et al.*, Phys. Rev. Lett. **73**, 3203 (1994)], relativistic stabilization of the $7s$ orbital leads to the ground state of 112^+ being $6d^9 7s^2$, rather than the $d^{10}s$ ground states of the lighter group 12 elements. The 112^{2+} ion shows very strong mixing of the d^8s^2, d^9s, and d^{10} configurations. The lowest state of the dication is $6d^8 7s^2$ $J=4$, with a very close (0.05 eV) $J=2$ state with strong d^8s^2 and d^9s mixing. No bound states were found for the anions of the two atoms.

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I. INTRODUCTION

Excitation energies and ionization potentials of the mercury atom have been the subject of many calculations in the past, using a variety of methods. Hafner and Schwartz [1] used a relativistic model potential fitted to the low excitation energies of Hg$^+$ and determined a large number of excitation energies of the neutral atom. Another model potential was used by Mohan and Hibbert [2] in the framework of the configuration-interaction (CI) method to calculate the $6s^2$ $^1S_0 \rightarrow 6s6p$ $^{1,3}P_1$ transitions. The latter have also been studied by Migdalek and co-workers [3–5] using multiconfiguration Hartree-Fock and CI methods and by Chou and Huang [6] with the relativistic random-phase approximation. More recently, Häussermann *et al.* [7] treated several states of Hg and its cation by the multireference CI method. All these calculations involved some form of model or pseudopotential. Häussermann *et al.* [7] also carried out all-electron Dirac-Fock calculations for comparison purposes, but such calculations do not include correlations and cannot be expected to yield results comparable to experiment. We are not aware of any all-electron calculations of the ionization potential or excitation energies of mercury, which includes both relativistic and correlation effects.

An accurate theoretical prediction of transition energies in heavy atoms requires high-order inclusion of both relativistic and correlation effects. An *ab initio* relativistic coupled-cluster (RCC) method incorporating both effects has been applied recently to a series of heavy atoms, including gold [8], several lanthanides and actinides [9,10], and elements 104 [11] and 111 [12]. Calculated transition energies were in very good agreement with known experimental values, usually within a few hundred wave numbers. Even higher accuracy was obtained for fine-structure splittings. The method is applied here to atomic mercury and ekamercury (element 112).

II. METHOD

The relativistic coupled-cluster method has been described in our previous publications [8,13] and only a brief review is given here. We start from the projected Dirac-Coulomb (or Dirac-Coulomb-Breit) Hamiltonian advocated by Sucher [14],

$$H_+ = H_0 + V, \tag{1}$$

where (in a.u.)

$$H_0 = \sum_i \Lambda_i^+ h_D(i) \Lambda_i^+ , \tag{2}$$

$$h_D(i) = c\boldsymbol{\alpha}_i \cdot \mathbf{p}_i + c^2(\beta_i - 1) + V_{\rm nuc}(i) + U(i), \tag{3}$$

$$V = \sum_{i<j} \Lambda_i^+ \Lambda_j^+ (V_{\rm eff})_{ij} \Lambda_j^+ \Lambda_i^+ - \sum_i \Lambda_i^+ U(i) \Lambda_i^+ . \tag{4}$$

Here h_D is the one-electron Dirac Hamiltonian. An arbitrary potential U is included in the unperturbed Hamiltonian H_0 and subtracted from the perturbation V. This potential is chosen to approximate the effect of the electron-electron interaction; in particular, it may be the Dirac-Fock self-consistent-field potential. The nuclear potential $V_{\rm nuc}$ includes the effect of finite nuclear size. Λ_i^+ are projection operators onto the positive energy states of the Dirac Hamiltonian h_D. Because of their presence, the Hamiltonian H_+ has normalizable, bound-state solutions. This approximation is known as the no-(virtual)-pair approximation, since virtual electron-positron pairs are not allowed in intermediate states. The form of the effective potential $V_{\rm eff}$ depends on the gauge used. In Coulomb gauge it becomes (in a.u., correct to second order in the fine-structure constant α) [15]

$$V_{\mathrm{eff}}=\frac{1}{r_{12}}+B_{12}+O(\alpha^3), \tag{5}$$

where the frequency-independent Breit interaction is

$$B_{12}=-\frac{1}{2r_{12}}[\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2+(\boldsymbol{\alpha}_1\cdot\mathbf{r}_{12})(\boldsymbol{\alpha}_2\cdot\mathbf{r}_{12})/r_{12}^2]. \tag{6}$$

In q-number theory the Dirac-Coulomb-Breit Hamiltonian H_+ is rewritten in terms of normal-ordered products of the spinor operators $\{r^+s\}$ and $\{r^+s^+ut\}$ [14,16]

$$H=H_+-\langle 0|H_+|0\rangle=\sum_{r,s} f_{rs}\{r^+s\}+\tfrac{1}{4}\sum_{r,s,t,u}\langle rs||tu\rangle \times\{r^+s^+ut\}, \tag{7}$$

where f_{rs} and $\langle rs||tu\rangle$ are, respectively, elements of one-electron Dirac-Fock and antisymmetrized two-electron Coulomb-Breit interaction matrices over Dirac four-component spinors. The effect of the projection operators Λ^+ is now taken over by the normal ordering, denoted by the curly brackets in the equation above, which requires annihilation operators to be moved to the right of creation operators as if all anticommutation relations vanish. The Fermi level is set at the top of the highest occupied positive energy state and the negative energy states are ignored.

The no-pair approximation leads to a natural and straightforward extension of the nonrelativistic open-shell coupled-cluster (CC) theory. The multireference valence-universal Fock-space coupled-cluster approach is employed here, which defines and calculates an effective Hamiltonian in a low-dimensional model (or P) space, with eigenvalues approximating some desirable eigenvalues of the physical Hamiltonian. According to Lindgren and Morrison's formulation of the open-shell CC method [17], the effective Hamiltonian has the form

$$H_{\mathrm{eff}}=PH\Omega P, \tag{8}$$

where Ω is the normal-ordered wave operator

$$\Omega=\{\exp(S)\}. \tag{9}$$

The excitation operator S is defined in the Fock-space coupled-cluster approach with respect to a closed-shell reference determinant. In addition to the traditional decomposition into terms with different total (l) number of excited electrons, S is partitioned according to the number of valence holes (m) and valence particles (n) to be excited with respect to the reference determinant

$$S=\sum_{m\geqslant 0}\sum_{n\geqslant 0}\left(\sum_{l\geqslant m+n} S_l^{(m,n)}\right). \tag{10}$$

The upper indices in the excitation amplitudes reflect the partitioning of the Fock space into sectors, which correspond to the different numbers of electrons in the physical system. This partitioning allows for partial decoupling of the open-shell CC equations, since the equations in each sector do not involve excitation amplitudes from higher sectors. The eigenvalues of the effective Hamiltonian (8) in a sector give directly the correlated energies in that sector with respect to the correlated (0,0) reference state. These transition energies may be ionization potentials, electron affinities, or excitation energies, according to the presence of valence holes and/or valence particles.

In the present application, we use the (0,0), (0,1), (0,2), (1,0), and (2,0) sectors. The lower index l in (10) is truncated at $l=2$. The resulting coupled cluster with single and double excitations (CCSD) scheme involves the fully self-consistent, iterative calculation of all one- and two-body virtual excitation amplitudes and sums all diagrams with these excitations to infinite order. Negative energy states are excluded from the Q space and the diagrammatic summations in the CC equations are carried out only within the subspace of the positive energy branch of the Dirac-Fock spectrum.

III. CALCULATIONS

The Fock-space relativistic coupled-cluster method was applied to several ionization states of the mercury and element 112 atoms. Two sequences of the open-shell CC calculations were carried out for Hg, starting from the closed-shell systems $\mathrm{Hg}^{2+}\ 5d^{10}$ or $\mathrm{Hg}\ 5d^{10}6d^2$, and then adding or removing electrons, respectively:

$$\mathrm{Hg}^{2+}(0,0)\rightarrow\mathrm{Hg}^{+}(0,1)\rightarrow\mathrm{Hg}(0,2), \tag{11}$$

$$\mathrm{Hg}(0,0)\rightarrow\mathrm{Hg}^{+}(1,0)\rightarrow\mathrm{Hg}^{2+}(2,0). \tag{12}$$

The ground state of the 112^{2+} ion is found to be $6d^87s^2$ rather than $6d^{10}$, in analogy with the 111^+ ion [12]. Only scheme (12) is therefore used.

The Dirac-Fock [16] and RCC [8,13] programs are both written for spherical symmetry, utilizing the angular decomposition of the wave function and CC equations in a central field. The energy integrals and CC amplitudes that appear in the Goldstone-type diagrams defining the CC equations are decomposed in terms of vector-coupling coefficients, expressed by angular-momentum diagrams, and reduced Coulomb-Breit or S matrix elements, respectively. The reduced equations for single and double excitation amplitudes are derived using the Jucys-Levinson-Vanagas theorem [17] and solved iteratively. This technique makes possible the use of larger basis sets.

To avoid "variational collapse" [18], the Gaussian spinors in the basis are made to satisfy kinetic balance [19]. They also satisfy relativistic boundary conditions associated with a

TABLE I. Basis sets for Hg and element 112. Members of the well- or even-tempered s-basis series used in the various l sectors are given.

Atom	Basis	Ref.	s	p	d	f	g	h
Hg	$31s26p23d16f10g6h$	[20]	1–31	5–30	8–30	11–26	15–24	18–23
112	$35s26p21d15f10g6h$	[21]	1–35	9–34	13–33	17–31	21–30	24–29

TABLE II. Ionization potential (IP) and excitation energies (EE) of Hg (cm^{-1}). PP, pseudopotential; HF, Hartree-Fock; MCHF, multiconfiguration Hartree-Fock; CI, configuration interaction; MCRRPA, multiconfiguration relativistic random-phase approximation; MRCI, multireference CI; AE-DF, all-electron Dirac-Fock; AE-RCC1, all-electron relativistic coupled cluster, starting from Hg^{2+}[Eq. (11)]; AE-RCC2, same, starting from Hg [Eq. (12)].

		IP ($6s^2$)	EE to $6s6p$			
Method	Ref.	${}^1S_0$	${}^3P_0$	${}^3P_1$	${}^3P_2$	${}^1P_1$
PP-HF	[1]	85681	34730	36722	41013	54571
PP-MCHF	[3]	80636		39040		54500
PP-CI	[2]		36410	38584	42819	53420
PP-CI	[4]	78673		34924		48363
PP-MCHF	[5]			37245		53903
PP-MCRRPA	[6]			33461		
PP-MRCI	[7]	82260	37738	39532	44062	53434
AE-DF	[7]		26422	28389	33655	
AE-RCC1		84521	37453	39302	44190	55453
AE-RCC2		84237				
Expt.	[22]	84184	37645	39412	44043	54069

finite nucleus, described here as a sphere of uniform proton charge [16]. The atomic masses used are 200.59 for Hg and 272 for element 112. The speed of light c is 137.03599 a.u. Nonrelativistic calculations are carried out by setting c to 10^5 a.u.

The uncontracted well-tempered basis set of Huzinaga and Klobukowski [20] was used for Hg and the universal basis set of Malli *et al.* [21] was selected for element 112. The basis sets, which go up to h orbitals ($l=5$), are summarized in Table I. Atomic orbitals with the same l but different k number (e.g., $p_{1/2}$ and $p_{3/2}$) are expanded in the same basis functions. Correlated shells include the $5s5p5d4f6s$ electrons of Hg and the $6s6p6d5f7s$ electrons of element 112. Virtual orbitals with high orbital energies have been found to contribute very little to correlation effects on excitation energies; orbitals higher than 100 a.u. are therefore eliminated from the calculation, effecting considerable savings in computational effort. All computations were carried out on the IBM RS6000/390 workstation at Tel Aviv University.

IV. RESULTS AND DISCUSSION

A. Hg

The ionization potential and excitation energies of mercury, calculated by schemes (11) and (12), are shown in Table II and compared with experiment [22] and with previous calculations [1–7]. The RCC results are more accurate than any previously reported. The average error in the five calculated energies is 380 cm^{-1}. With the exception of the ${}^1P_1$ excitation, they are all within 200 cm^{-1} of experiment. The only calculation of comparable accuracy is that of Häussermann *et al.*, [7] using energy-adjusted pseudopotentials with multireference CI (PP-MRCI) in the valence shell.

Table III shows transition energies in the Hg^+ and Hg^{2+} ions. Very good agreement with experiment is obtained for the low-lying levels of both ions. The very high (above 12 eV) $5d^86s^2$ levels of Hg^{2+} are not reproduced as well. The most likely reason is the incompleteness of the basis. The PP-MRCI method [7] does not perform very well for the ions, giving errors of 1000–2000 cm^{-1} even for the low excitation energies.

B. Element 112

Ionization potentials and excitation energies of element 112 and its ions, calculated by scheme (12) with the neutral atom as reference, are shown in Table IV. The ground state of the monocation is $6d^97s^2\ {}^2D_{5/2}$ rather than $d^{10}s$, the

TABLE III. Ionization potential (IP) and excitation energies (EE) of Hg^+ and Hg^{2+} (cm^{-1}). Methods and references as in Table II.

State			Expt.	AE-RCC1	AE-RCC2	PP-MRCI	AE-DF
			Hg^+, ground state $5d^{10}6s\ {}^1S_{1/2}$				
IP			151280	151200	150435	150580	
EE	$5d^96s^2$	${}^2D_{5/2}$	35514		35437	34350	37374
		${}^2D_{3/2}$	50552		50785	48782	51984
	$5d^{10}6p$	${}^2P_{1/2}$	51485	52030			
		${}^2P_{3/2}$	60608	61269			
			Hg^{+2}, ground state $5d^{10}\ {}^1S_0$				
EE	$5d^9({}^2D_{5/2})6s$	${}^3D_3$	42850		43715	41664	43393
		${}^3D_2$	46030		46854	44818	47445
	$5d^9({}^2D_{3/2})6s$	${}^3D_1$	58406		59630	56459	58539
		${}^1D_2$	61086		62192	59610	62793
	$5d^86s^2$	$J=4$	97894		101014		
		$J=2$	106028		109683		
		$J=3$	112226		115724		
		$J=2$	118927		122791		
		$J=0$	122661		122509		
		$J=1$	122735		126857		
		$J=4$	126468		130881		
		$J=2$	133732		138178		

TABLE IV. Ionization potentials and excitation energies of element 112 and its ions (cm^{-1}). DC, Dirac-Coulomb Hamiltonian; DCB, Dirac-Coulomb-Breit Hamiltonian, including the term (6).

	State		DC	DCB
	112, ground state $6d^{10}7s^2\ ^1S_0$			
IP			96721	96545
	112$^+$, ground state $6d^97s^2\ ^2D_{5/2}$			
IP			181143	181420
EE	$6d^{10}7s$	$^2S_{1/2}$	13330	12896
	$6d^97s^2$	$^2D_{3/2}$	26058	25363
	112^{2+}, ground state $6d^87s^2$ $J=4$			
EE	$6d^87s^2,6d^97s$	$J=2$	567	374
	$6d^9(^2D_{5/2})7s$	$^3D_3$	1941	1493
	$6d^{10},6d^87s^2$	$^1S_0$	7034	6411
	$6d^97s,6d^87s^2$	$J=2$	11579	11228
	$6d^87s^2,6d^{10}$	$^1S_0$	25719	25351
	$6d^87s^2$	$J=3$	25885	25165
	$6d^9(^2D_{3/2})7s$	$^3D_1$	29536	28353
	$6d^97s,6d^87s^2$	$J=2$	30039	29196
	$6d^87s^2$	$J=1$	35171	34451
	$6d^87s^2,6d^97s$	$J=2$	37185	36161
	$6d^87s^2$	$J=4$	38462	37742

TABLE V. Energy differences of d^9s and d^{10} levels in Au [8], element 111 [12], Hg$^+$, and the 112$^+$ ion (eV).

Transition	Au	111	Hg$^+$	112$^+$
$^2S_{1/2}$-$^2D_{5/2}$	−1.15	2.95	−4.39	1.60
$^2S_{1/2}$-$^2D_{3/2}$	−2.67	0.26	−6.30	−1.54
$^2D_{3/2}$-$^2D_{5/2}$	1.52	2.69	1.91	3.14

ground state of Hg$^+$ and other elements of group 12. The switch is due to the relativistic stabilization of the $7s$ orbital relative to the $6d$. A similar phenomenon has been observed for the isoelectronic element 111 [12]. Table V compares energy differences in the d^9s and d^{10} configurations of Au and element 111 with the isoelectronic Hg$^+$ and 112$^+$ ion. Large changes occur both in the group 11 atoms and group 12 monocations upon going from the lighter to the heavier species. These changes, ascribed mostly to relativistic effects, are larger in the cations than in the neutral species. Thus the $^2S_{1/2}$-$^2D_{5/2}$ difference increases by 4.1 eV when going from Au to element 111; the corresponding increase in the Hg$^+$-112$^+$ pair is 6.0 eV. The larger effect is probably due to the contraction of orbitals in the cations relative to neutral atoms, bringing them closer to the nucleus and enhancing relativistic effects. This interpretation is corroborated by the fine-structure splittings of the ^2D level in Hg$^+$ and the 112$^+$ ion, which are significantly larger than in Au and element 111.

The dications of Hg and element 112 also show large differences in level ordering. The ground-state configuration of Hg^{2+} is $5d^{10}$, with the lowest states of $5d^96s$ and $5d^86s^2$ much higher (5.3 and 12 eV, respectively). The order is reversed in ekamercury, with the three configurations rather close in energy. While the calculated ground state is $6d^87s^2$ with $J=4$, the next level (with $J=2$) is only 0.05 eV higher and might conceivably become the ground state in a more accurate treatment. The $J=2$ level shows very strong mixing of the d^8s^2 and d^9s configurations and is pushed below the $J=3$ level. Other cases of strong configuration mixing occur, involving either the d^8s^2 and d^9s pair or (for the two $^1S_0$ levels) the $6d^87s^2$ and $6d^{10}$ configurations. The most important configurations contributing to the various levels are indicated in Table IV. The levels themselves are designated only by their J values, except for the few cases where an LS designation is appropriate.

V. SUMMARY AND CONCLUSION

Ionization potentials and excitation energies were calculated for Hg and element 112, and for their mono- and dications. Very good agreement with experiment is obtained for the Hg transition energies, with the exception of the high (>12 eV) excitation energies of the dication. In analogy with element 111 [12], relativistic stabilization of the $7s$ orbital leads to the ground state of the 112$^+$ ion being $6d^97s^2$ rather than the $d^{10}s$ ground states of the lighter group 12 elements. Relativistic effects in the 112$^+$ ion are even stronger than in element 111. Very strong mixing of the d^8s^2, d^9s, and d^{10} configurations occurs in the 112^{2+} ion. The lowest state of the dication is $6d^87s^2$ $J=4$, but a very close (0.05 eV) $J=2$ state with strong d^8s^2 and d^9s mixing cannot be ruled out as a possible ground state. Finally, it should be noted that we could not find a bound anion of either Hg or element 112.

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